BROWN

The Replacement of Tin Oxide by Antimony Oxide in Enamels for Cast Iron

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THE REPLACEMENT OF TIN OXIDE BY ANTIMONY OXIDE IN ENAMELS FOR CAST IRON

BY

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THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

Mr. R. E. Brown

ENTITLED The Replacement of Tin Oxide by Antimony Oxide in Enamels for Cast Iron.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF B. S. in Ceramics.

A. V. Bleininger
Instructor in Charge

APPROVED: A. V. Bleininger

HEAD OF DEPARTMENT OF Ceramics.

The value of the cast iron enamel as it is employed today depends largely on its ability to cover up a rough and otherwise unattractive surface in such a way as to prevent corrosion, to give it a pleasing and attractive appearance, as well as to present a smooth glassy cover which may be easily and effectively cleaned. In order to bring this about it is necessary to compound a mixture which has a fusion point within workable limits, i.e. below the weakening point of cast iron and yet above that point where the enamel is of such a nature as to be insoluble in water and dilute solutions of acids.

In order to obtain a suitable enamel it is necessary to obtain a glassy coating or cover which possesses such a coefficient of contraction as to permit it to adhere to the metal, and in which is held some substance which gives the enamel opacity. These latter substances are known as opacifiers, and for the purposes of this work are divided into two classes: (1) partial opacifiers and (2) absolute opacifiers.

In the first class are included bone ash, fluorite, cryolite and silica. Bone ash is rarely employed in enamels, but the remaining three, especially the silica, are invariably used. Fluorite and cryolite are advantageous, commercially, both from the standpoint of their low fusibility and their fluorine content, but also as weak opacifiers, thereby decreasing the amount of absolute opacifier needed.* The silica as is shown by the follow-

*Mayer and Havas. Sprechsaal 42, 460-461.

ing work has no opacifying tendencies in itself in this type of glasses but emphasizes and increases the opacity brought about by certain opacifiers, proper.

Under the second class, the opacifiers per se are, arsenious oxide, zirconium oxide, tin oxide and antimony oxide. Arsenious oxide finds only a very limited use, it being employed only for decorative work on jewelry and art ware. Zirconium oxide is not widely used and while some consider it too expensive for commercial work, others regard it as a cheap opacifier as a substitute for tin oxide.* Tin oxide is by far the most widely used of the opacifiers, and is employed not only in the enamelling of sheet iron and cast iron, but in the enamelling of clay products as well.

Antimony oxide has had, to date, only an extremely limited use as an opacifier. It has been used to some extent in Germany in conjunction with zinc oxide as a substitute for tin oxide.** It has been used in this country to some extent, and in one case its use in conjunction with other ingredients is patented as "A substitute for tin oxide".° In a "Note on White Antimony Enamels", Bock points out the dangers of the use of antimony oxide in enamels for cooking vessels, but no mention is made of its employ-

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*La Ceramique, 11, 100 - 101.

Keram Rundschau, 16, 89 - 91; 135 - 139.

**Ph. Eyer, Stahl and Eisen, 28, 1097, 1099.

°U. S. Patent, 932, 839.

ment in enamels for cast iron.*

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*Chem. Ztg. 32, 516-517.

The most expensive constituent of the ordinary commercial enamel is the opacifying agent, Tin Oxide, both by reason of the high market price, and the quantity employed. The prices of antimony oxide and tin oxide in barrel lots are 10 1/2¢ and 45¢ per pound respectively.

OBJECT OF WORK.

It was with a view to using the cheaper opacifier for cast iron enamels that this work was undertaken. The work attempts to determine, in a practical way, the conditions under which antimony oxide may be used in enamels.

The work was divided into groups so as to show separately the effect of some of the more important ingredients of the enamels.

OUTLINE OF WORK.

A. Execution of work.

a. Preparation of Enamels.

b. The Trial Pieces.

c. Function and Composition of the Ground Coats.

d. Burning the Enamels.

e. The Ingredients.

f. The Starting Point.

B. Series I. Replacement of Tin Oxide by Antimony Oxide in a Tin Enamel.

C. Series II. Variation of Barium Oxide and its effect on Antimony Oxide.

D. Series III. Variation of Silica Content.

E. Series IV. Variation of Alumina.

F. Series V. Variation of Antimony Oxide with two contents of Silica (1.8 and 2.0 equivalents).

G. Series VI. Replacement of Antimony Oxide by Tin Oxide in an Antimony Enamel (using two equivalents of Silica 1.8 and 2.0 equivalents).

H. Series VII. Variation of Boric Oxide with two contents of Silica (1.8 and 2.0 equivalents).

EXECUTION OF WORK.

(a) Preparation of the Enamels.

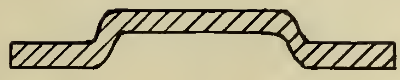
In carrying out a series the ingredients of the two extremes of a series were weighed up and mixed thoroughly by passing 5 or 6 times through a 20 mesh screen. The batch was next put into a small fire clay crucible (capacity about 250 grams of the raw batch) and fritted in a pot furnace fired by a blast lamp using artificial gas and compressed air as fuel. After melting and becoming relatively free from bubbles the contents were poured into water. It was then dried and again put into the crucibles and refritted, care being taken in this second fritting to prolong the heating to such a length of time that no bubbles were given off. As soon as bubbles had ceased to form the contents were again quenched by pouring into water. The shattered glass was dried and then ground in 8 inch porcelain ball mills so as to pass a 200 mesh

sieve.

The two extremes of a series, now in a powdered form were weighed out in the proper proportions, i.e. in the ratio of their combining weights, to form the intermediate enamels. These two parts were now mixed by rubbing 5 or 6 times through a 60 mesh sieve.

(b) The Trial Pieces.

The trial pieces were small circular discs 1/8" thick and 2" in diameter with a raised center as shown by diagram. The iron



Section through Trial

used for casting these trials did not prove to be of a very satisfactory grade as it frequently produced large bubbles or blisters in the enamels probably due to the sulphur content of the iron.

The trials were cleaned by pickling for 20 - 30 minutes in a dilute solution of hydrochloric acid so as to remove the scale and any oxide present. After this they were washed and scrubbed and then dipped in a dilute solution of sodium carbonate so as to neutralize all of the acid. They were then scrubbed and washed again, the surface water wiped off, and put into a previously warmed oven. Even with this seemingly thorough treatment, the coat of carbon (left by dissolving the iron) was not entirely removed, and hence gave rise to bubbles during the burning process. Another method of cleaning the iron, used in the later part of the work, proved very effective. In this the iron was pickled as before and then put into a ball mill with sand and water thus effectually removing

all of the carbon, with the result that less trouble as regards bubbling was experienced.

After drying, the ground coat was applied to the trials. This was done by dipping, care being taken to secure a thin coat, which was as uniform as possible.

(c) Function and Composition of the Ground Coats.

The first ground coat used was of the composition as shown below. It is similar to that quoted by Eyer, Chem. Ztg. 32, 516 - 517, except the addition of clay and tin oxide on grinding:

$$\left.\begin{array}{ll} .064 & \text{Cao} \\ .37 & Na_2O \\ .19 & K_2O \\ .075 & PbO \\ .28 & MgO \end{array}\right) \quad \left.\begin{array}{ll} .21 & Al_2O_3 \\ .379 & B_2O_3 \end{array}\right) \quad 1.43\ SiO_2$$

Batch weights: 13.25 Flint; 26.6 Potash Spar; 14.7 Boric Acid; 3.1 Borax; 4.8 Soda Ash; 4.5 KNO_3; 5.8 Red Lead; 2. $CaCO_3$; 8.5 $MgCO_3$; 11.2 Cryolite; 0.2 Fluorspar.

This ground coat was too soft and was changed to one of the following composition:

$$\left.\begin{array}{ll} .117 & CaO \\ .225 & K_2O \\ .066 & PbO \\ .353 & MgO \\ .212 & Na_2O \end{array}\right) \quad \left.\begin{array}{ll} .228 & Al_2O_3 \\ .238 & B_2O_3 \end{array}\right) \quad 1.7\ SiO_2$$

Batch weights: 16.8 Flint; 33.7 Potash Spar; 11.2 Boric Acid; 5.6 KNO_3; 5.6 Red Lead; 3.4 $CaCO_3$; 11.2 $MgCO_3$; 11.2 Cryolite;

1.1 Fluorspar.

This ground coat did not fuse as readily as the first one and did not give as much trouble as regards bubbling. A ground coat quoted by Cheney, Vol. XII Trans. Amer. Cer. Soc. of the formula,

$$\left.\begin{array}{l} .45\ K_2O \\ .55\ Na_2O \end{array}\right) \quad \left.\begin{array}{l} .55\ Al_2O_3 \\ .7\ \ B_2O_3 \end{array}\right) \quad 2.9\ SiO_2$$

in which the ingredients were borax, china clay, potash spar, and soda ash, was also tried, but was too soft for this work.

The ground finally chosen was of the composition shown:

$$\left.\begin{array}{ll} .30 & K_2O \\ .24 & Na_2O \\ .159 & CaO \\ .219 & MgO \\ .081 & PbO \end{array}\right) \quad \left.\begin{array}{ll} .297 & Al_2O_3 \\ .31 & B_2O_3 \end{array}\right) \quad 2.19\ SiO_2$$

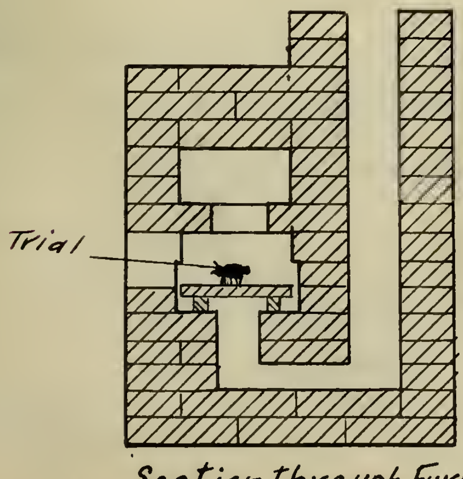
Batch weights: 15 Flint; 30 Potash Feldspar; 10 Boric Acid; 5 KNO_3; 5 Pb_3O_4; 2.2 $Ca(OH)_2$; 2.3 MgO; 10.0 Cryolite; 1.0 Fluorite.

The trial piece after being slush coated and dried was placed in the furnace which had already been heated to the temperature of burning. As soon as the iron had attained a sufficient heat for fusing the ground enamel, it appears to "melt" not unlike to that of a coat of frost or snow. This commences at one spot and soon has extended over the whole trial. The trial now has a glossy appearance. Almost coincident with this, innumerable bubbles are formed which "break" at once. This continues for a short time after which the glossy coating or gloss smoothes down. It is at this

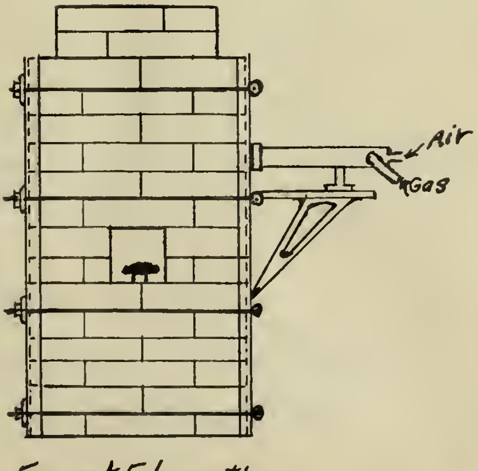
point, in the writers judgment, that the burning of the ground coat is complete. If the trial is not removed at once, larger bubbles are formed and these are decidedly more viscous than the preliminary bubbles. When they break, if they break at all, they leave a rough slag on the surface of the trial as is shown by cooling the trial piece.

(d) Burning the Enamels.

The furnace used for the enamelling was one belonging to the Geology Department. It was of the open fired type, i.e. without a muffled chamber, and was fired using artificial gas and compressed air as fuel. Although this is not the type of furnace best suited for this kind of work, it was the only one available and there was no time for the construction of a more suitable one. The temperature of burning was measured by a Le Chatelier pyrometer the couple of which was inserted so that its junction point was at the side of the trial. A sketch of the furnace showing the position of the trial and the construction of the furnace is given below. The holder for the trial piece consisted of a bar of iron "upset" at one end and so shaped as to fit on the inside of the trial piece.



Section through Furnace



Front Elevation

The trial piece to which the ground coat had been previously applied was placed in the chamber and left for about three minutes or until the ground coat had reached the proper state of fusion. It was then removed and the powdered enamel sifted on through an 80 mesh screen. Since the trial pieces were so small that they cooled rapidly in the air, it was necessary to go through this operation once more, the trial of course being heated up between these two operations, so that the part of the coat already applied fused down. In some cases it was necessary to make three applications of the enamel. The time for burning a thickness of enamel was about 30 seconds hence the trial was held on the holder until matured. As soon as burned the trials were set aside in the open air to cool. It must be understood that the successful burning of enamels is controlled by several factors, e.g. application of the enamel, condition of the iron, temperature of burning, duration of burning, the condition of the matured ground coat and the character of the fire gases. In case a trial is held in a trifle too long, bubbling occurs and if drawn too soon it is rough and dull. From this it will be seen that in an experimental way, results are often obtained that would not otherwise occur under proper conditions.

(e) The Ingredients.

The raw materials employed in introducing the constituents are as follows:

ZnO - Introduced as zinc oxide.

PbO - Brought in as red lead, Pb_3O_4. This form is preferable to the white lead owing to its oxidizing value $2\ Pb_3O_4 =$

6 PbO + O_2, this reaction occurring about 550° C.

BaO - Where employed was brought in by using barium carbonate.

CaO - Brought in as Fluorite, Whiting and Hydrated CaO.

Na_2O - Introduced as Sodium Carbonate and Borax.

K_2O - Brought in as Potassium Nitrate and Potash Feldspar.

MgO - Brought in as Magnesium Carbonate and Magnesium oxide.

Al_2O_3 - Potash spar was used mainly as a source of Al_2O_3. Small amounts of cryolite were also used.

B_2O_3 - This was brought in by using borax in the cover enamels and as borax and boric acid in the ground coats.

SnO_2 - Brought in as tin oxide.

Sb_2O_3 - Introduced as white oxide of antimony.

SiO_2 - Brought in as potash spar and as flint.

In addition to the above ingredients, ammonium carbonate was used in some of the enamels of the later series. This volatilizes readily and serves as a clarifier of bubbles in the glass during fritting.

(f) The Starting Point.

As a starting point in this work an enamel similar to that given by Riddle in his "Types of Enamels for Enamelling Cast Iron Sanitary Ware", Trans. A. C. S. Vol. IX. is taken as a basis. The formula is as follows:

$$\left.\begin{array}{ll} .25 & Na_2O \\ .1 & MgO \\ .15 & PbO \\ .15 & BaO \end{array}\right\} \left.\begin{array}{ll} .15 & Al_2O_3 \\ .2 & B_2O_3 \end{array}\right) \begin{array}{ll} 1.0 & SiO_2 \\ .15 & SnO_2 \end{array}$$

$$\left.\begin{array}{l} .15\ K_2O \\ .05\ ZnO \\ .15\ CaO \end{array}\right)$$

The batch corresponding to the above formula was weighed up (excluding the tin oxide), fritted, quenched in water, the necessary tin oxide added, and the whole ground to pass a 200 mesh screen. It was then applied to a trial piece as described under "Burning the Enamels". It fused easily but was of a gray color being, however, bright and glossy. The next step was to fritt the tin oxide with the whole batch and repeat the above process. This gave a good enamel much improved in opacity and general appearance.

B. Series I.

Replacement of Tin Oxide by Antimony Oxide in a Tin Enamel.

This series was carried out by replacing the tin oxide in the enamel above (in which the tin oxide was weighed in before fritting) with antimony oxide, thus:

$$\left.\begin{array}{l} .25\ Na_2O \\ .1\ \ MgO \\ .15\ PbO \\ .15\ BaO \\ .15\ K_2O \\ .05\ ZnO \\ .15\ CaO \end{array}\right) \quad \left.\begin{array}{l} .15\ Al_2O_3 \\ .2\ \ B_2O_3 \end{array}\right) \quad \begin{array}{l} 1.0\ SiO_2 \\ \ .15\ SnO_2 - .075\ Sb_2O_3 \end{array}$$

In giving the batch composition of an enamel it is tabulated as a batch formula, expressed in equivalents of the different ingredients. Thus the make up of the batch may be shown

more closely than by the usual general formula.

Batch Formulae (in equivalents)

No.	Na_2CO_3	R.Lead	$BaCO_3$	CaF_2	ZnO	$MgCO_3$	Borax	K.Spar	Flint	SnO_2	Sb_2O_3
1	.15	.05	.15	.15	.05	.1	.1	.15	.1	.15	0
2	.15	.05	.15	.15	.05	.1	.1	.15	.1	.1125	.0188
3	.15	.05	.15	.15	.05	.1	.1	.15	.1	.075	.0375
4	.15	.05	.15	.15	.05	.1	.1	.15	.1	.0375	.056
5	.15	.05	.15	.15	.05	.1	.1	.15	.1	0	.075

Description of Trials: Number 1 is a good enamel and is a typical tin enamel. All the rest of the series with the possible exception of Number 2 are very poor. A peculiar "puckery" or matte texture exists, the surface is rough and uneven; and the enamel flies off in patches resembling shivering of clay ware. In the trials of enamels 3 and 4, the puckery effect is partially overcome by raising the burning temperature. The shivering is also lessened by this treatment. It was also evident in this series as well as in the rest of the work that where an enamel is applied too think shivering is more likely to occur.

Thinking perhaps that the "puckery" effect might be overcome partially by making a more easily fusible enamel it was decided to run a series with a more fusible RO combination. It was also suggested that the "puckery" effect might be due to the barium which reacted with the sulphur present in the Sb_2O_3.* Some

*Sb_2O_3 is prepared from stibnite Sb_2S_3 by roasting in air, hence sulphates are formed which if not entirely removed would combine with the barium compounds.

of the Sb_2O_3 was tested and found to contain sulphur.

A series embodying the two above ideas was accordingly carried out as given below. Although it was not conducted strictly on a scientific basis it is sufficient to show in a practical way the desired effect.

C Series II.

Variation of Barium Oxide and its effect on Antimony Oxide.

.25 - .54 Na_2O	.15 - .16 Al_2O_3	1.0 SiO_2
.1 - .0 MgO	.2 B_2O_3	.075 Sb_2O_3
.15 - .15 PbO		
.15 - .16 K_2O		
.05 - .05 ZnO		
.15 - .1 CaO		
.15 - .0 BaO		

Batch Formulae (in equivalents)

No.	Na_2CO_3	R. Lead	$BaCO_3$	CaF_2	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	$MgCO_3$	Spar	Flint	Sb_2O_3
1	.15	.05	.15	.15	.05	.0	.0	.0	.1	.1	.15	.1	.075
2	.21	.05	.10	.1	.05	.02	.02	.03	.1	.07	.148	.14	.075
3	.29	.05	.05	.05	.05	.04	.04	.07	.1	.03	.136	.18	.075
4	.35	.05	.0	.0	.05	.06	.06	.1	.1	.0	.13	.22	.075

Description of Trials: The puckery effect has decreased toward the end of the series which contains no barium and in No. 4 is not present at all. This enamel is a fair enamel which adheres

well. No. 1 is somewhat shivered. This series shows from a practical standpoint that Barium should not be used to any very large extent in an enamel where there is a contact with sulphur gases. Its use however in enamels where tin is used as an opacifier is very much desired owing to its ability to decrease shivering.

D Series III.

Variation of the Silica Content.

This series was varied between the limits of 1.0 and 2.0 equivalents of silica as shown:

$$\left.\begin{array}{l} .1\ CaO \\ .54\ Na_2O \\ .15\ PbO \\ .16\ K_2O \\ .05\ ZnO \end{array}\right) \left.\begin{array}{l} .16\ Al_2O_3 \\ .2\ B_2O_3 \end{array}\right) \begin{array}{l} 1.0 - 2.0\ SiO_2 \\ .075\ Sb_2O_3 \end{array}$$

Batch Formulae (in equivalents)

No.	Na_2CO_3	R.Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K.Spar	Flint	Sb_2O_3
1	.35	.05	.05	.06	.06	.1	.1	.13	.22	.075
2	.35	.05	.05	.06	.06	.1	.1	.13	.345	.075
3	.35	.05	.05	.06	.06	.1	.1	.13	.47	.075
4	.35	.05	.05	.06	.06	.1	.1	.13	.595	.075
5	.35	.05	.05	.06	.06	.1	.1	.13	.72	.075
6	.35	.05	.05	.06	.06	.1	.1	.13	.845	.075
7	.35	.05	.05	.06	.06	.1	.1	.13	.97	.075
8	.35	.05	.05	.06	.06	.1	.1	.13	1.095	.075
9	.35	.05	.05	.06	.06	.1	.1	.13	1.22	.075

Description of Trials: No. 1, 2 and 3 have an egg shell like texture but otherwise are fair enamels. The trials of enamels No. 4 and 5 are better and do not show the above texture to such a degree. No. 6 is a fair enamel but is a trifle dull. No. 7 is a good enamel and adheres well. It is whiter and has a better gloss than the average commercial enamel. Enamel No. 8 is whiter than No. 7 and has a better gloss. A few of the trials shiver somewhat, showing that the silica is a trifle too high. Enamel No. 9 has shivered still more but on the trials where it held it is the whitest and most brilliant of the series. Enamels No. 8 and 9 have an exceptionally white color and are more than the equal of the average tin enamel in this respect.

The results of this series seem to show that the last two enamels are too high in silica and also that a silica content of over 1.85 equivalents is conducive to shivering. The burning temperature rises as the silica content increases but this heat even with the enamels containing 2.0 SiO_2 did not deteriorate the iron to any visible extent. As silica increases the whiteness is increased and it is evident that a sacrifice must be made of part of the whiteness in order to obtain enamels that do not shiver.

E Series IV.
Variation of Alumina

This series was run between the limits of .1 and .2 equivalents of Al_2O_3. To bring in the Al_2O_3 in combined form, i.e. as spar, it was necessary to change the ratio with respect to K_2O and Na_2O, thus:

$$\left.\begin{array}{l} .16 - .2\ K_2O \\ .15\ PbO \\ .1\ CaO \\ .54 - 5\ Na_2O \\ .05\ ZnO \end{array}\right) \begin{array}{l} .1 - .2\ Al_2O_3 \\ 0.2\ B_2O_3 \end{array} \left.\vphantom{\begin{array}{l}a\\b\end{array}}\right) \begin{array}{l} 1.8\ SiO_2 \\ .075\ Sb_2O_3 \end{array}$$

Batch Formulae (in equivalents)

No.	Na_2CO_3	R. Lead	ZnO	K_2CO_3	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K.Spar	Flint	Sb_2O_3
1	.35	.05	.05	.06	.06	.06	.1	.1	.07	1.38	.075
2	.342	.05	.05	.049	.06	.06	.1	.1	.09	1.26	.075
3	.334	.05	.05	.038	.06	.06	.1	.1	.11	1.14	.075
4	.326	.05	.05	.025	.06	.06	.1	.1	.13	1.02	.075
5	.318	.05	.05	.013	.06	.06	.1	.1	.15	.90	.075
6	.31	.05	.05	.0	.06	.06	.1	.1	.17	.78	.075

Description of Trials: All enamels of the series are good enamels with whiteness increasing toward No. 6 i.e. with increase of Al_2O_3. The temperature required for maturing increases however with the Al_2O_3. The best enamel of the series taking burning temperature whiteness, gloss and adhesive properties into consideration is No. 4 containing .16 Al_2O_3.

F Series V.

VARIATION OF ANTIMONY OXIDE

This series as well as the remaining two series was carried out in two parts, A and B, the two parts being practically alike except for the silica content. Part B was carried out first and the limits of Sb_2O_3 were not high enough, hence was changed in A.

V B Batch Formulae (in equivalents)

No.	Na_2CO_3	R.Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K.Spar	Flint	Sb_2O_3
1	.35	.05	.05	.06	.06	.1	.1	.13	1.22	.0
2	.35	.05	.05	.06	.06	.1	.1	.13	1.22	.022
3	.35	.05	.05	.06	.06	.1	.1	.13	1.22	.044
4	.35	.05	.05	.06	.06	.1	.1	.13	1.22	.066
5	.35	.05	.05	.06	.06	.1	.1	.13	1.22	.088
6	.35	.05	.05	.06	.06	.1	.1	.13	1.22	.11

Series V A

$$\left.\begin{array}{ll} .16 & K_2O \\ .05 & ZnO \\ .1 & CaO \\ .15 & PbO \\ .54 & Na_2O \end{array}\right) \quad \begin{array}{l} .16\ Al_2O_3 \\ .2\ B_2O_3 \end{array} \left.\right) \quad \begin{array}{l} 1.8\ SiO_2 \\ 0 - .14\ Sb_2O_3 \end{array}$$

Series V B

$$\left.\begin{array}{ll} .16 & K_2O \\ .05 & ZnO \\ .1 & CaO \\ .15 & PbO \\ .54 & Na_2O \end{array}\right) \quad \begin{array}{l} .16\ Al_2O_3 \\ .2\ B_2O_3 \end{array} \left.\right) \quad \begin{array}{l} 2.0\ SiO_2 \\ 0 - .11\ Sb_2O_3 \end{array}$$

V A. Batch Formulae (in equivalents)

No.	Na_2CO_3	R.Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K.Spar	Flint	Sb_2O_3
1	.35	.05	.05	.06	.06	.1	.1	.13	1.02	.0
2	.35	.05	.05	.06	.06	.1	.1	.13	1.02	.02
3	.35	.05	.05	.06	.06	.1	.1	.13	1.02	.04
4	.35	.05	.05	.06	.06	.1	.1	.13	1.02	.06
5	.35	.05	.05	.06	.06	.1	.1	.13	1.02	.08
6	.35	.05	.05	.06	.06	.1	.1	.13	1.02	.10
7	.35	.05	.05	.06	.06	.1	.1	.13	1.02	.12
8	.35	.05	.05	.06	.06	.1	.1	.13	1.02	.14

Description of Trials: The trials of enamel A 1 have but slight opacity. No. 2 A has a trifle more and so on up the series. Enamel No. 3 A has a fair opacity, No. 4 A and 5 A are good enamels,

No. 5 A being the whitest. No. 6 A is a good enamel. It is whiter than No. 5 but is not quite as glossy. No. 7 is a good enamel and is a trifle "matte" in texture. No. 8 has a beautiful matte texture and differs from all the rest of the series in this respect. One of the trials however shows a slight tendency to shiver but this may possibly be due to the mode of application. Enamel No. 5 is the best of the A part of the series taking gloss, finish and general appearance into consideration while for a dull or matte texture No. 8 is the best. Enamels No. 7 and 8 require a higher temperature for burning, thus indicating that high antimony decreases the fusibility.

With part B of the series shivering is more evident in every case. The enamels which held however are of greater brilliancy and opacity, enamel No. 2 of A being identical in appearance with No. 1 of B. Enamels 2, 3 and 4 of part B are practically the same as 3, 4 and 5 of part A respectively. From this we would conclude that .016 equivalents of Sb_2O_3, in this range of silica content, have about the same opacifying effect as .02 equivalents of silica.

G Series VI.

Replacement of Antimony Oxide by Tin Oxide in an Antimony Enamel.

This series, also using two different equivalents of silica, was carried out as follows:

VI A

$$\left.\begin{matrix} .16\ K_2O \\ .05\ ZnO \\ .1\ CaO \\ .15\ PbO \\ .54\ Na_2O \end{matrix}\right) \quad \left.\begin{matrix} .16\ Al_2O_3 \\ .2\ B_2O_3 \end{matrix}\right) \quad \begin{matrix} 1.8\ SiO_2 \\ .075\ Sb_2O_3 - .15\ SnO_2 \end{matrix}$$

VI B

$$\left.\begin{matrix} .16\ K_2O \\ .05\ ZnO \\ .1\ CaO \\ .15\ PbO \\ .54\ Na_2O \end{matrix}\right) \quad \left.\begin{matrix} .16\ Al_2O_3 \\ .2\ B_2O_3 \end{matrix}\right) \quad \begin{matrix} 2.0\ SiO_2 \\ .075\ Sb_2O_3 - .15\ SnO_2 \end{matrix}$$

VI A Batch Formulae (in equivalents)

No.	Na_2CO_3	R. Lead	ZnO	KnO_3	Cryolite	$Ca(OH)_2$	Borax	K.Spar	Flint	Sb_2O_3	SnO_2
1	.35	.05	.05	.03	.06	.1	.1	.13	1.02	.075	.0
2	.35	.05	.05	.03	.06	.1	.1	.13	1.02	.056	.038
3	.35	.05	.05	.03	.06	.1	.1	.13	1.02	.038	.075
4	.35	.05	.05	.03	.06	.1	.1	.13	1.02	.019	.1125
5	.35	.05	.05	.03	.06	.1	.1	.13	1.02	.0	.15
		VI B									
1	.35	.05	.05	.03	.06	.1	.1	.13	1.22	.075	.0
2	.35	.05	.05	.03	.06	.1	.1	.13	1.22	.056	.038
3	.35	.05	.05	.03	.06	.1	.1	.13	1.22	.038	.075
4	.35	.05	.05	.03	.06	.1	.1	.13	1.22	.019	.1125
5	.35	.05	.05	.03	.06	.1	.1	.13	1.22	.0	.15

Description of Trials: All enamels of the A part of the series adhere tenaciously and are good enamels. Enamel No. 1 has more opacity and whiteness than No. 5, these two properties decreasing uniformly between these extremes. The antimony enamel requires a slightly higher temperature for maturing but not to such an extent as to be detrimental to the iron.

In the B part of the series shivering is much in evidence due to the increased silica. Enamels No. 1 and 2 have good opacity but numbers 3 and 4 are much inferior in this respect. In enamel No. 5 the silica has dissolved the SnO_2 almost entirely. Taking the results of this series we would conclude that SiO_2 at the higher limit is opposite in effect with regard to Sb_2O_3 and SnO_2. In the case of Sb_2O_3 the opacity, whiteness and brilliancy are increased, while with SnO_2 these properties, notably the opacity, are decreased. Shivering however is increased in either case. The results obtained in part A of the series are not in accord with those of Riddle whose high limit of silica was 1.25 equivalents. In enamel No. 5 part A as given above, a good white enamel was obtained using 1.8 equivalents of silica.

It might be interesting to note also at this point, the behavior of the enamels on wrought iron. The enamels of part A were applied to iron washers, and although they had not been previously cleaned, the enamels held perfectly and were of good whiteness, brilliancy and texture.

H Series VII.

Variation of Boric Oxide.

This series employs two equivalents of silica and the

and the Na_2CO_3 content is varied in order to reach the lower limit of B_2O_3 still maintaining the same ratio.

VII A.

$$\left.\begin{array}{ll} .16 & K_2O \\ .05 & ZnO \\ .1 & CaO \\ .15 & PbO \\ .54 & Na_2O \end{array}\right) \begin{array}{l} .16\ Al_2O_3 \\ .1 - .4B_2O_3 \end{array} \left.\right) \begin{array}{l} 1.8\ SiO_2 \\ .075\ Sb_2O_3 \end{array}$$

VII B.

$$\left.\begin{array}{ll} .16 & K_2O \\ .05 & ZnO \\ .1 & CaO \\ .15 & PbO \\ .54 & Na_2O \end{array}\right) \begin{array}{l} .16\ Al_2O_3 \\ .1 - .4B_2O_3 \end{array} \left.\right) \begin{array}{l} 2.0\ SiO_2 \\ .075\ Sb_2O_3 \end{array}$$

VII A Batch Formulae (in equivalents)

No.	Na_2CO_3	R.Lead	ZnO	KNO_3	Cryolite	$Ca(CH)_2$	Borax	K.Spar	Flint	Sb_2O_3
1	.4	.05	.05	.03	.06	.1	.05	.13	1.02	.075
2	.375	.05	.05	.03	.06	.1	.075	.13	1.02	.075
3	.350	.05	.05	.03	.06	.1	.10	.13	1.02	.075
4	.325	.05	.05	.03	.06	.1	.125	.13	1.02	.075
5	.300	.05	.05	.03	.06	.1	.150	.13	1.02	.075
6	.275	.05	.05	.03	.06	.1	.175	.13	1.02	.075
7	.25	.05	.05	.03	.06	.1	.2	.13	1.02	.075

VII B.

No.	Na_2CO_3	R.Lead	ZnO	KNO_3	Cryolite	$Ca(OH)_2$	Borax	K.Spar	Flint	Sb_2O_3
1	.4	.05	.05	.03	.06	.1	.05	.13	1.22	.075
2	.375	.05	.05	.03	.06	.1	.075	.13	1.22	.075
3	.350	.05	.05	.03	.06	.1	.1	.13	1.22	.075
4	.325	.05	.05	.03	.06	.1	.125	.13	1.22	.075
5	.300	.05	.05	.03	.06	.1	.150	.13	1.22	.075
6	.275	.05	.05	.03	.06	.1	.175	.13	1.22	.075
7	.250	.05	.05	.03	.06	.1	.200	.13	1.22	.075

Description of Trials: All enamels of part A adhere well and are good white enamels up to No. 6. Nos. 6 and 7 have a yellowish cast and are not at all desirable enamels. Bubbling is also evident in the enamels of higher B_2O_3 content. Enamel No. 1 is the whitest of the five enamels.

The results obtained in part B are substantially the same as those of part A. The enamels are whiter however than the ones of the same B_2O_3 content and the yellowish cast of enamels 6 and 7 of part A has disappeared in the corresponding enamels of part B. Shivering however is present to quite a large extent in part B due to the high silica. As in part A bubbling is prominent in the enamels of the higher B_2O_3 content. The difference in whiteness of the high and low B_2O_3 enamels in part A is not so pronounced in this part of the series. Enamels B 1 and B 7 have very little difference in whiteness, No. B 1 being a little the whitest. The difference in maturing temperature is however quite large and the tendency to bubbling is more evident.

The results indicate that the lower the B_2O_3 the better and whiter are the enamels. The limits for desirable enamels are

about .15 - .3 B_2O_3.

Limits of the Ingredients.

The limits of the ingredients and their effects established by this work are as follows:

SiO_2: The effect of silica is to increase brilliancy, whiteness, acid resisting properties and gloss. If increased too high shivering takes place and the maturing temperature is too high. The limits of silica are about 1.65 - 1.85 equivalents, those nearer the higher limit being preferable.

Al_2O_3: Increased Al_2O_3 increases the temperature for maturing and gives whiter enamels. The high limit is around .18 equivalents. The low limit was not established but for commercial enamels is probably about .13 equivalents.

Sb_2O_3: The effect of Sb_2O_3 is to increase the maturing temperature and to increase the whiteness and opacity when employed between the limits of 0 - .09 equivalents Sb_2O_3. If used between the limits of .1 - .14 equivalents the enamels are dull at the lower limits and increase to mattness at the higher. At the high limit, .14 equivalents, shivering is likely to occur.

For brilliant enamels of good opacity and texture the limits are .06 - .09 equivalents, about .075 being preferable.

SnO_2: No variation of the SnO_2 content was made but a good enamel was obtained using 0.15 equivalents of SnO_2.

B_2O_3: The effect of increased B_2O_3 is to lower the maturing temperature, to increase the tendency to produce bubbles, to decrease the whiteness when used above a certain limit, increase

gloss, and to increase the solubility of the enamel. The limits are about .15 - .3 equivalents, those nearer the lower limit being preferable.

PbO: No extensive work was carried out with this ingredient, but what results were obtained show that an enamel containing no PbO differs very little in whiteness and fusibility from those that did, thus showing that leadless Sb_2O_3 enamels can be produced.

BaO: The effect of BaO in Sb_2O_3 enamels is to produce a "puckery" or matte effect. This is no doubt due to the sulphur a-rising from the Sb_2O_3 and the fuel gases, which comes in contact with the Barium compounds.

The most likely enamel taking all points into consideration is:

$$\left.\begin{array}{ll} .16 & K_2O \\ .05 & ZnO \\ .1 & CaO \\ .15 & PbO \\ .54 & Na_2O \end{array}\right) \quad \left.\begin{array}{ll} .16 & Al_2O_3 \\ .2 & B_2O_3 \end{array}\right) \quad \begin{array}{ll} 1.8 & SiO_2 \\ .075 & Sb_2O_3 \end{array}$$